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04180290 15.06.1992
04180292 15.06.1992

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B6J JMG2 J501 J707
C3L LJE L130
H1X X5G
U1S S1156 S1540 S1632 S1635 S1654 S1845

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EP 0171239 A1 EP 0046945 A1 US 4724508 A

(58) Field of search
UK CL (Edition K) C3L LJE LJX, H1D DGP DGQ, H1X X5G
INT CL[5] C08J, H01J, H01T, H05H

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(54) Method and apparatus for surface treatment

(57) An object (4) is subjected to a surface treatment by locating it in an atmospheric pressure plasma i.e. at 200 torr – 3 atm., while rolling or floating the object (4) in an insulating vessel (1) fed with a prescribed gas and provided on the outside thereof or on both the outside and inside thereof with electrodes (2a, 2b) which are used to form the atmospheric pressure plasma. Thus uniform surface treatment of any object in the form of lump or sphere or powder is obtained.

For example, vulcanized rubber can be surface treated with an atmospheric pressure plasma in the presence of an oxygen-containing gas and halogen containing gases to improve its adhesion properties. Numerous different electrode configurations and different gas fillings for forming the atmospheric pressure glow discharge are disclosed. As shown, the object 4 may roll down an inclined tube 1, the tube itself may be reciprocated so that the object rolls back and forth, Fig. 11 (not shown). Alternatively, the object may float up and down in a vertical tube having a hinged flap at one end, Fig. 12 (not shown). The inner electrodes may also form supports along which the objects roll, Figs 32, 33 (not shown). The objects may also be located on a moving belt, Figs 13, 14 (not shown).

FIG.10

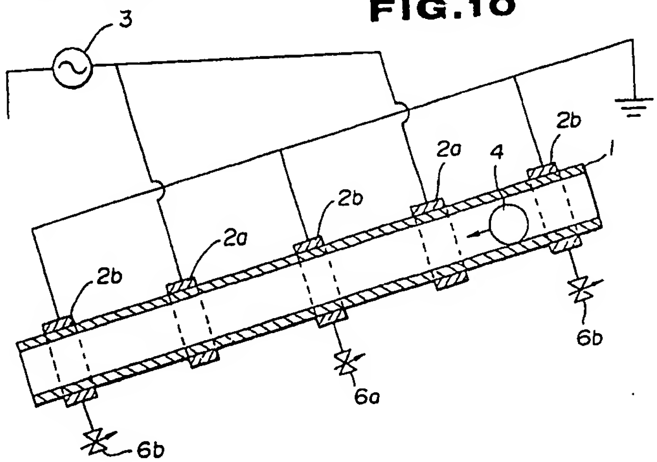

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FIG.1

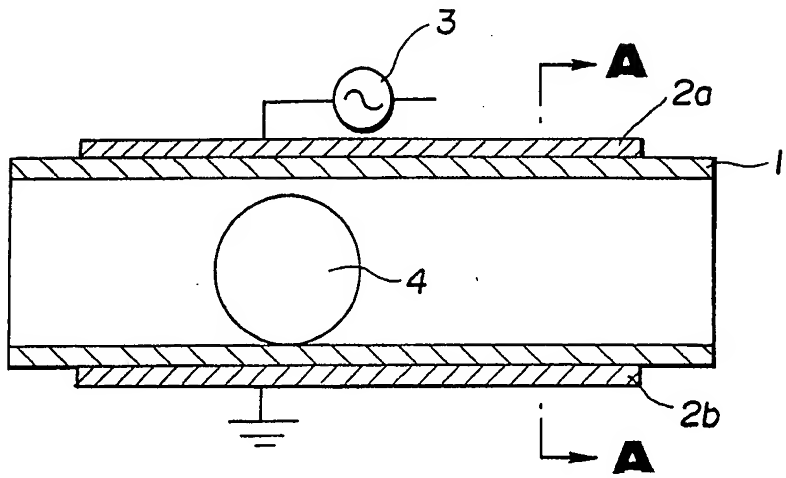

FIG.2

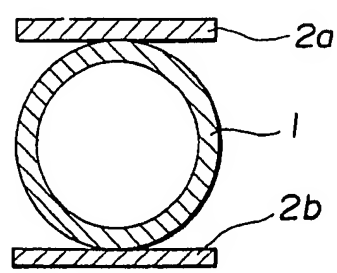

FIG. 3

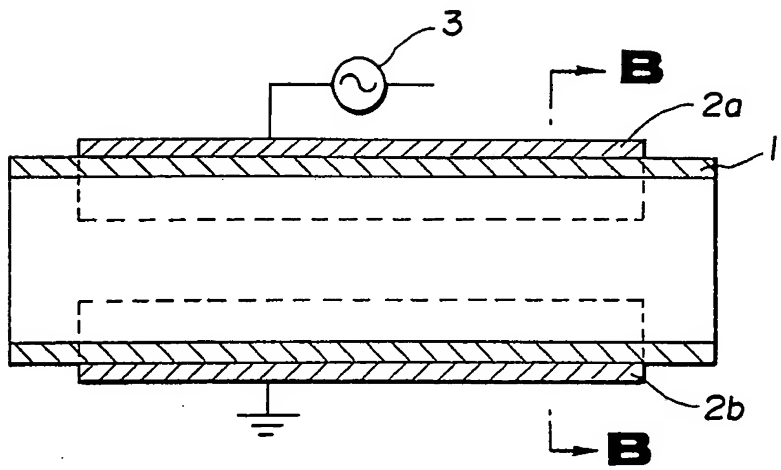

FIG. 4

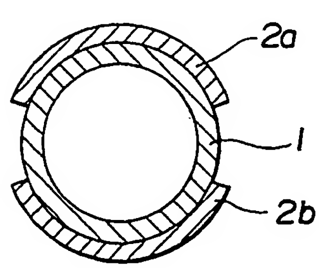

FIG. 5

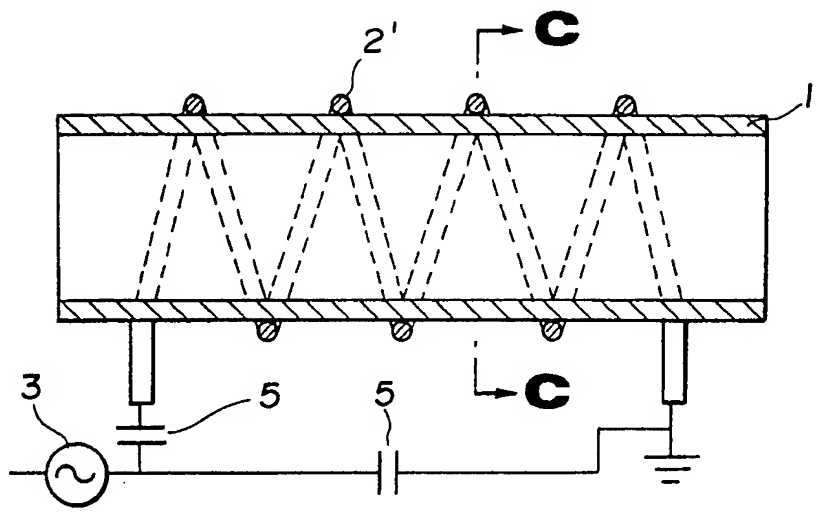

FIG. 6

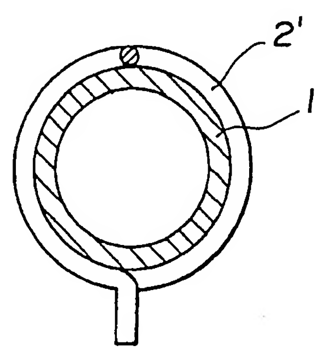

FIG.7

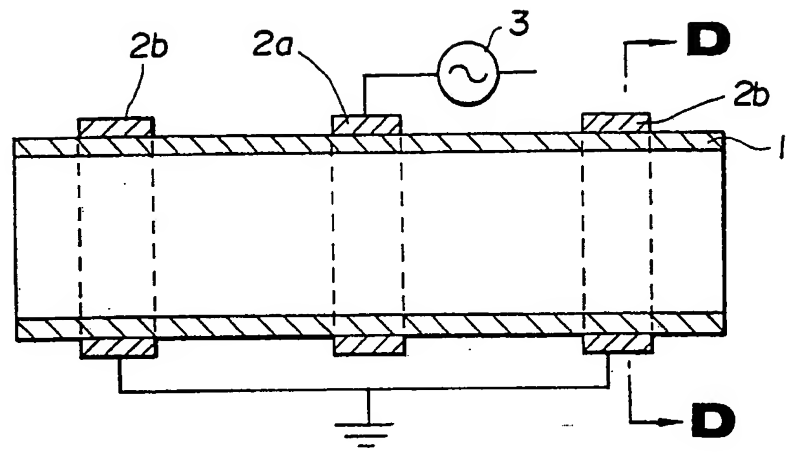

FIG.8

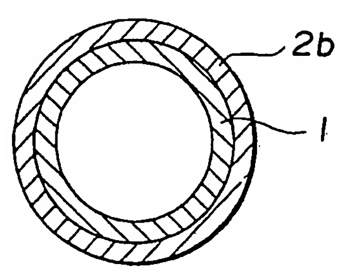

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FIG. 9

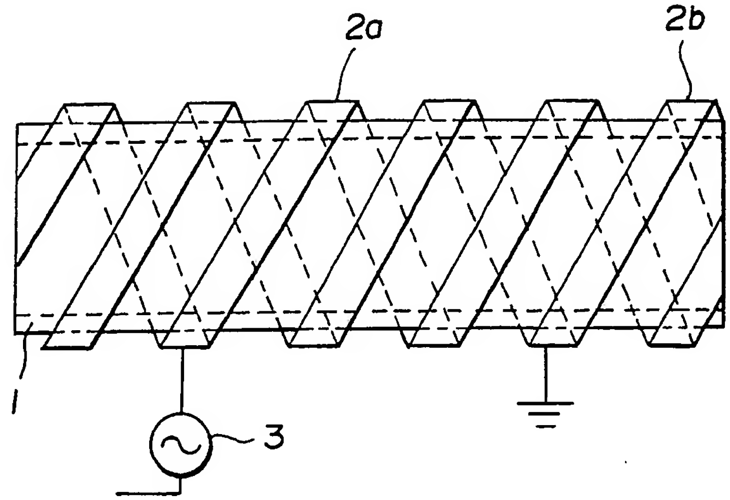


FIG. 10

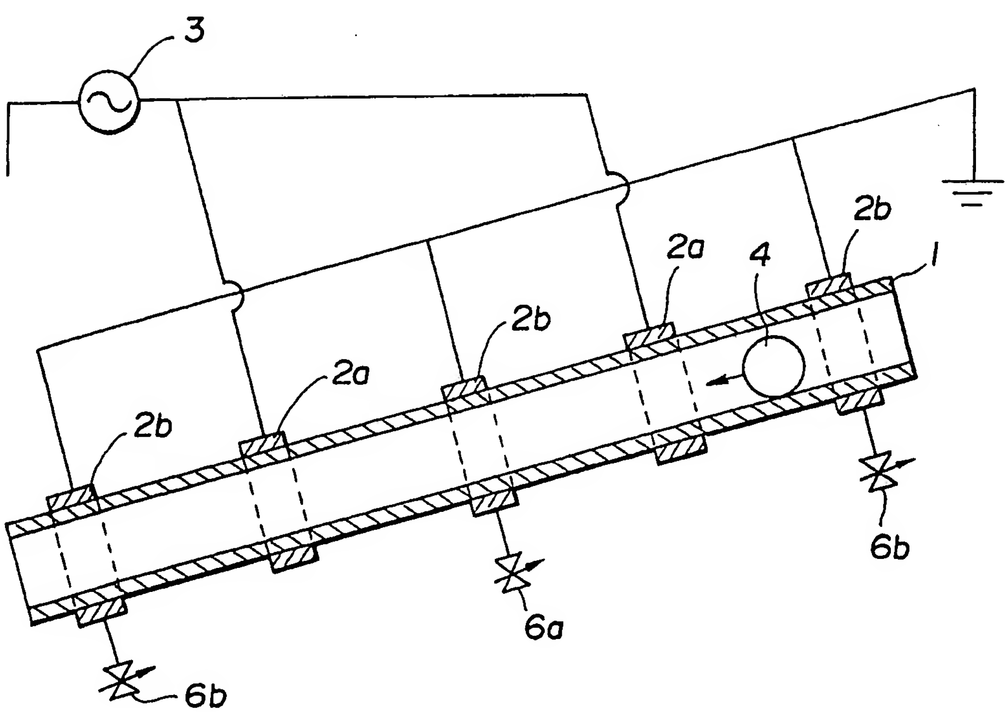
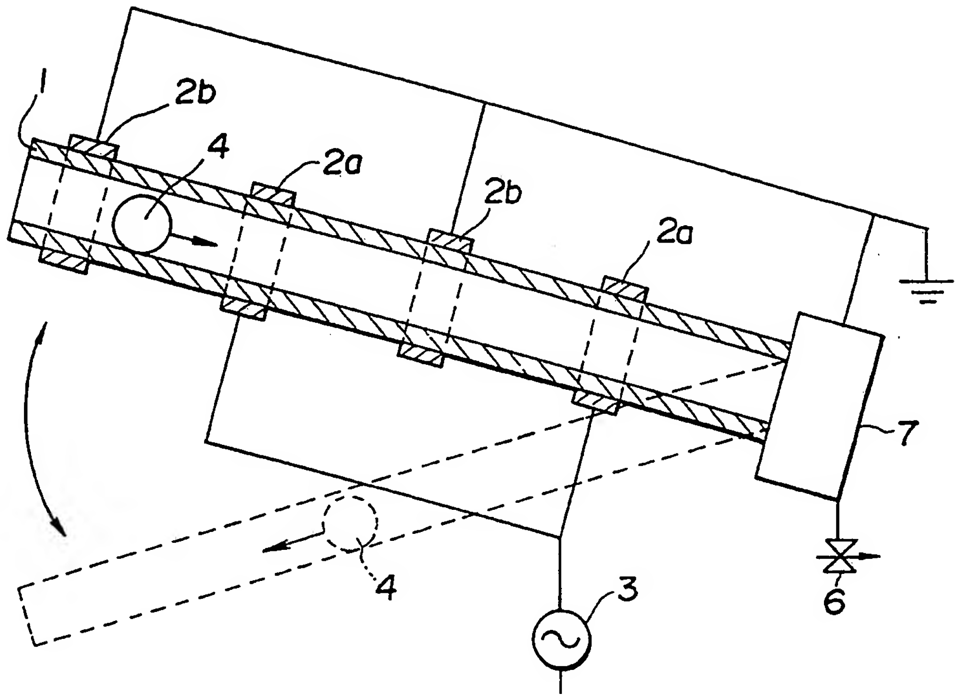


FIG.11



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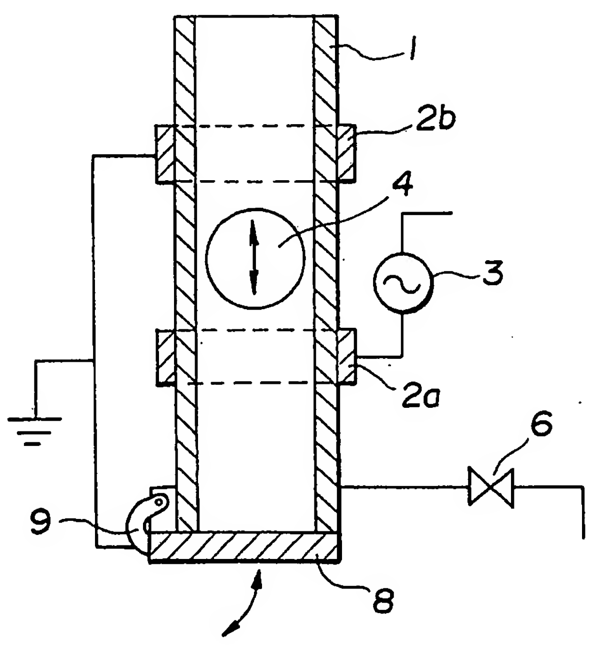
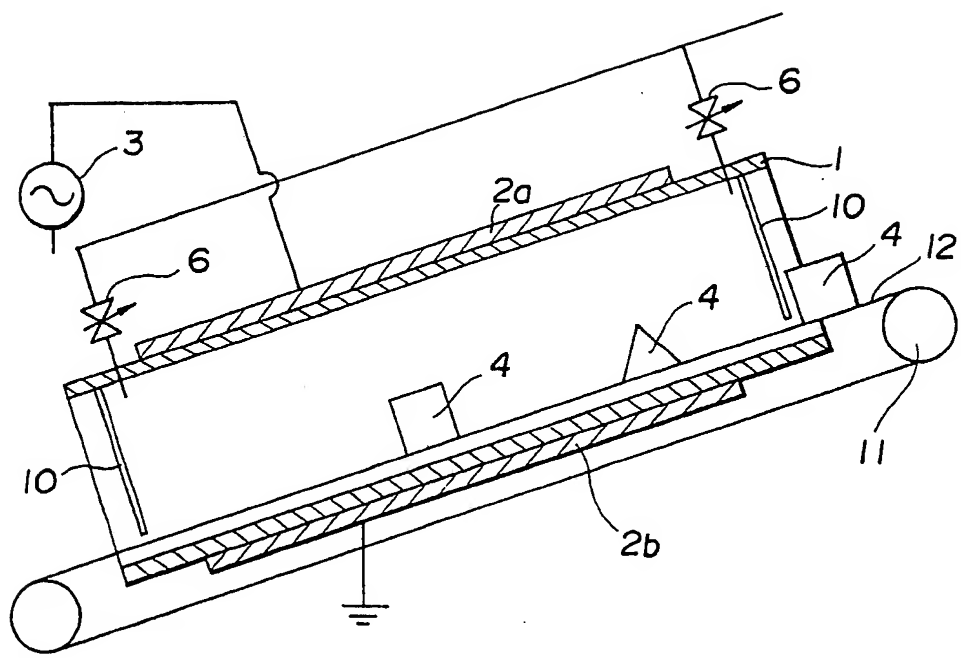


FIG.13



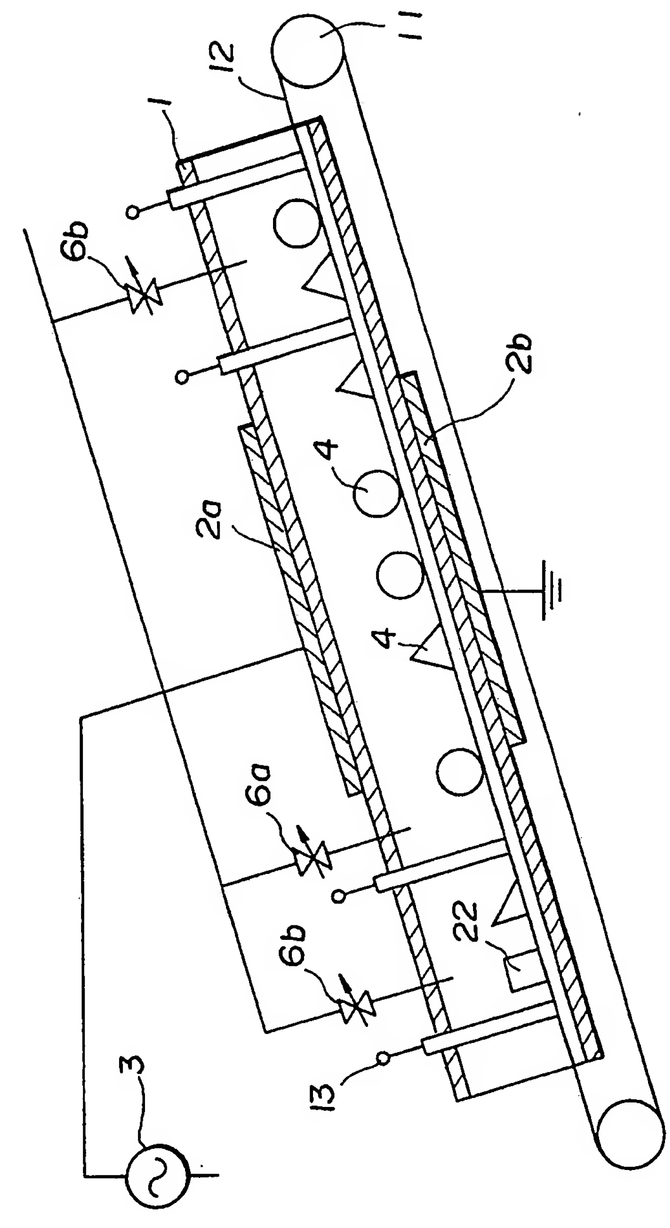


FIG.14

FIG.15

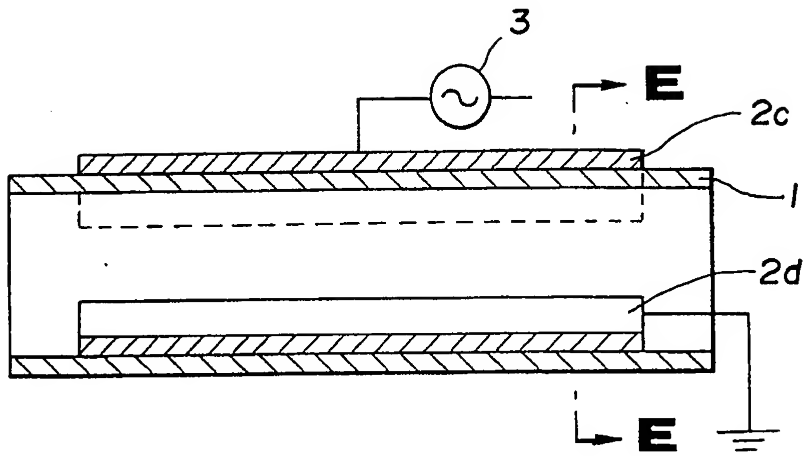


FIG.16

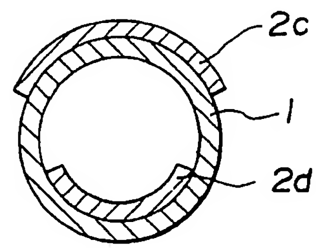


FIG.17

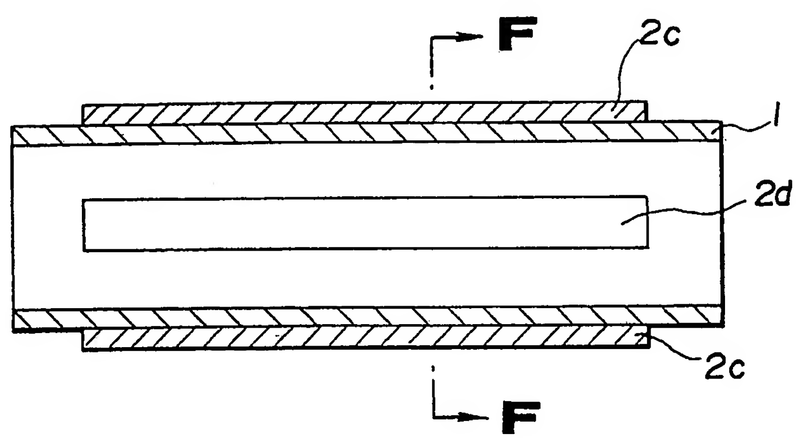


FIG.18

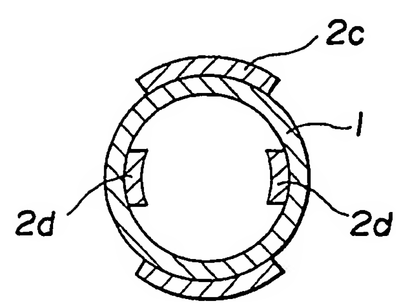


FIG.19

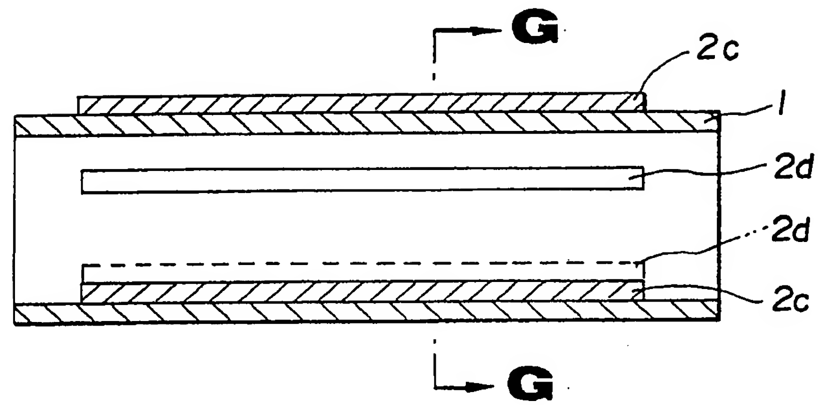


FIG.20

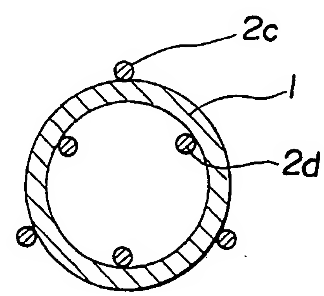


FIG.21

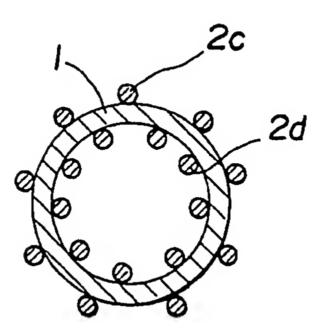


FIG.22

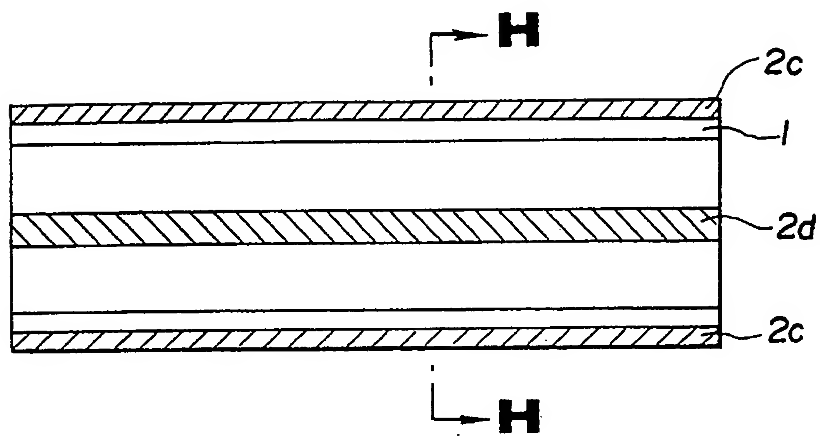


FIG.23

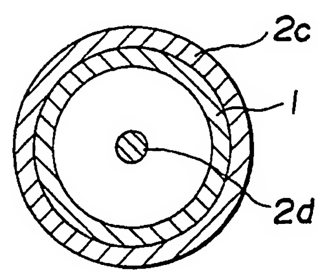
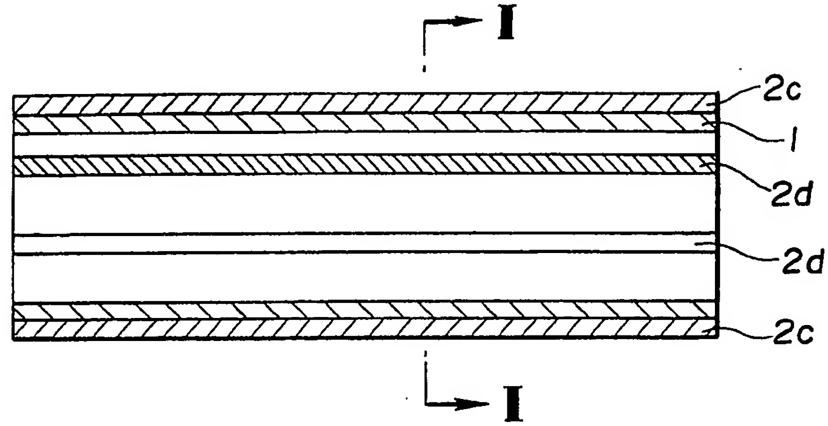


FIG.24



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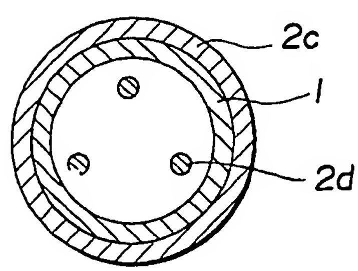


FIG. 26

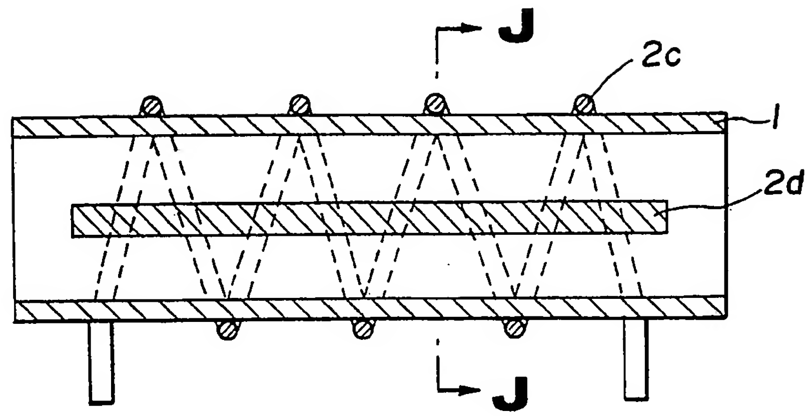


FIG. 27

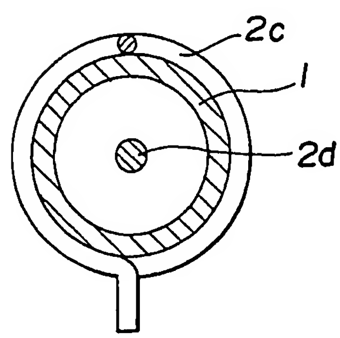


FIG.28

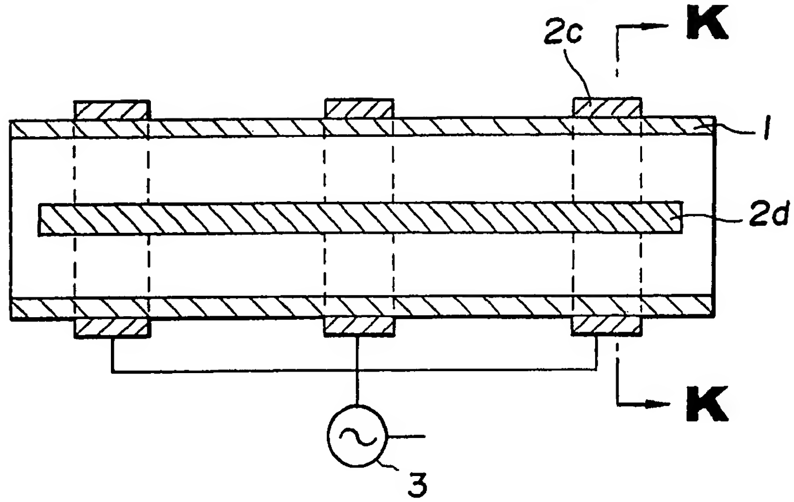


FIG.29

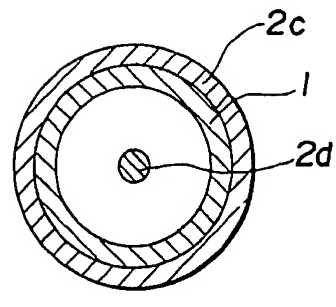


FIG.30

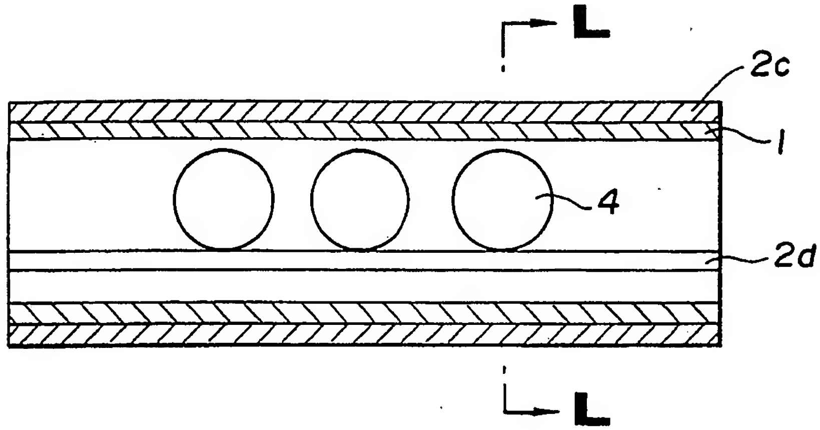


FIG.31

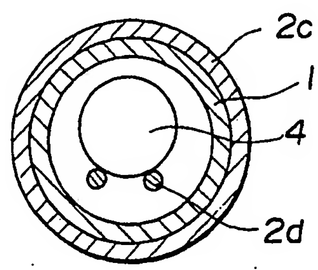


FIG. 32

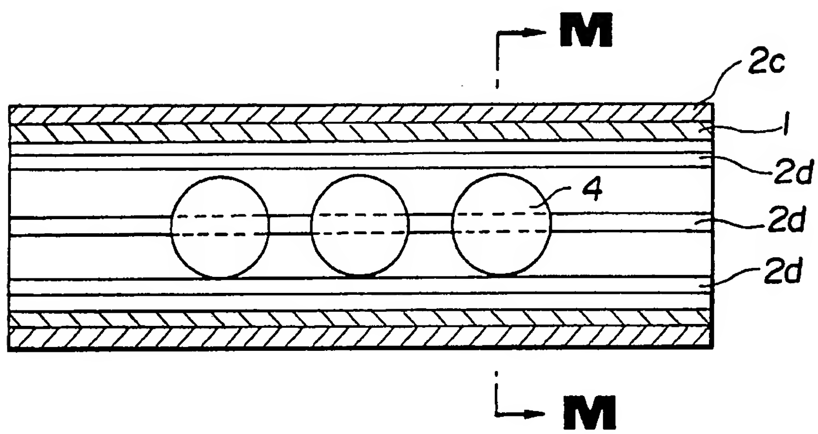


FIG. 33

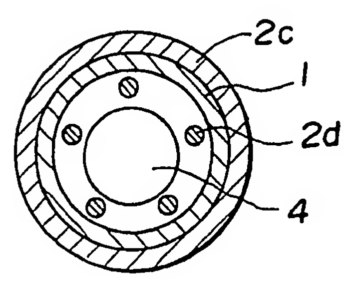


FIG. 34

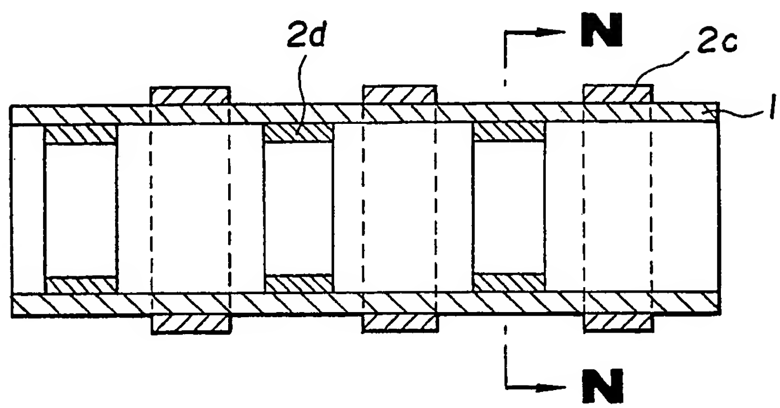


FIG. 35

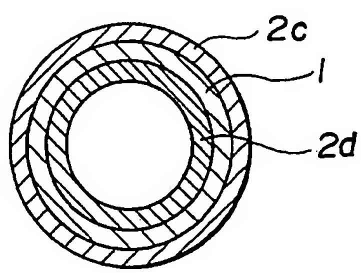


FIG. 36

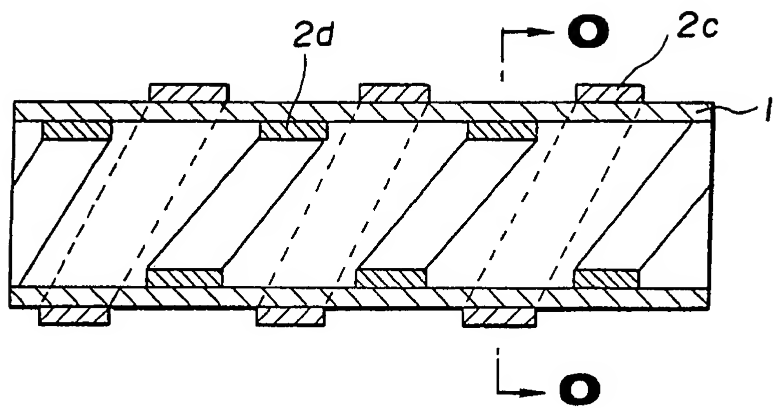


FIG. 37

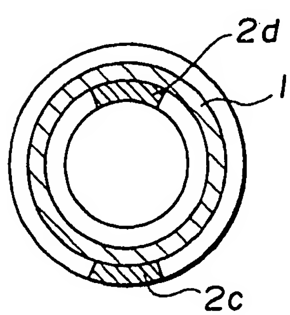


FIG. 38

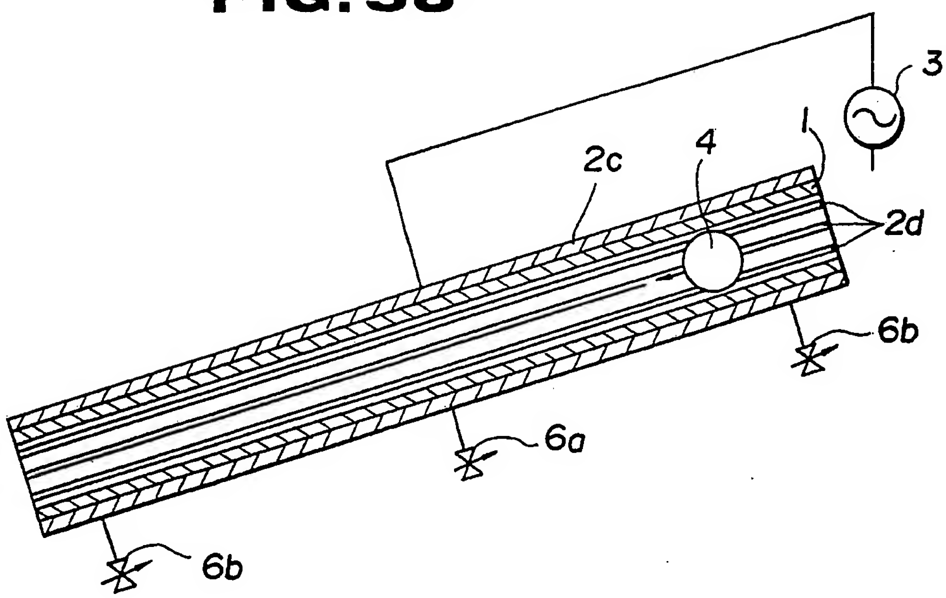


FIG. 39

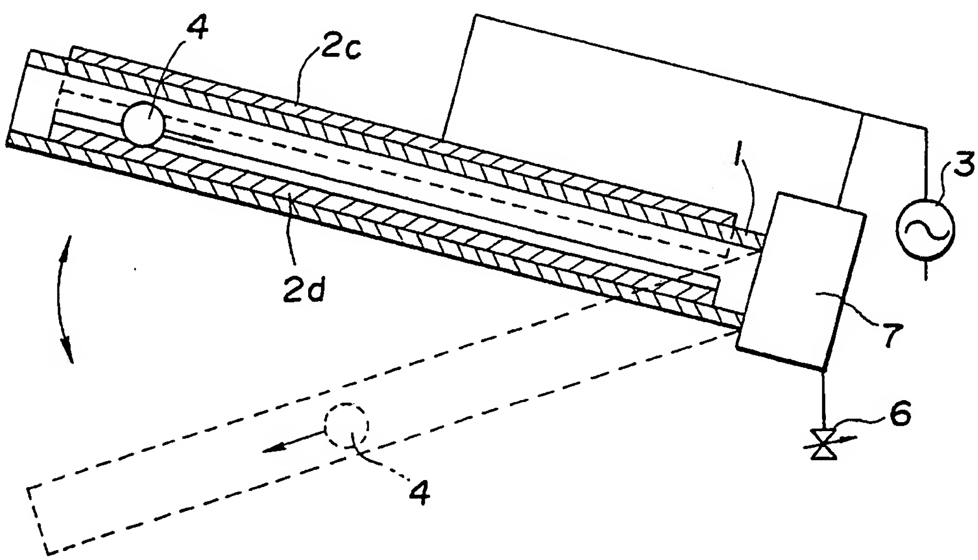


FIG.40

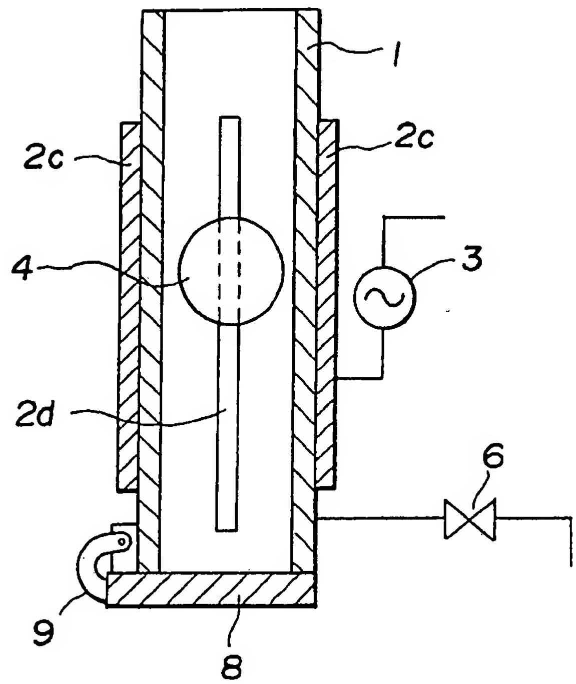


FIG.41

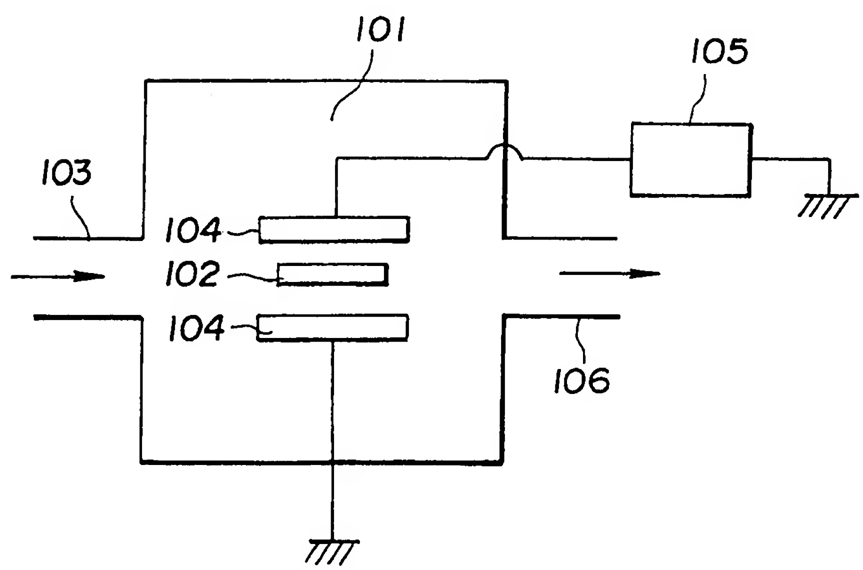
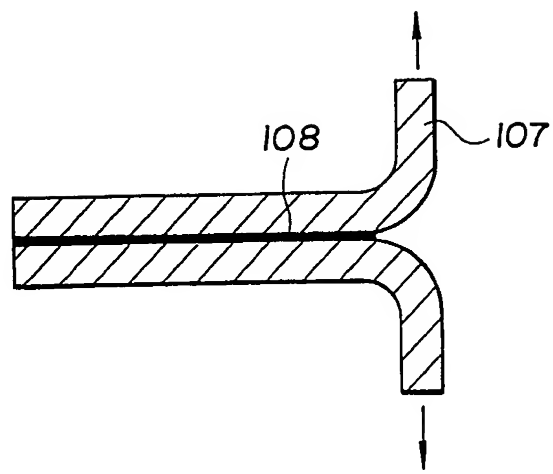


FIG. 42



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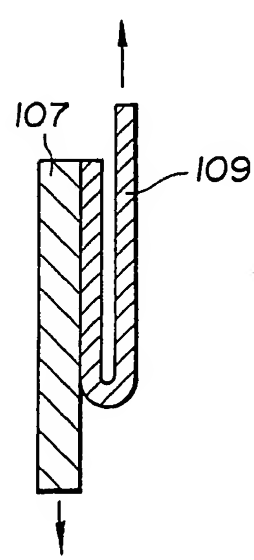

METHOD AND APPARATUS FOR SURFACE TREATMENT

The present invention relates to a method and apparatus for surface-treating any object in the form of lump, sphere, or powder with an atmospheric pressure plasma.

The present invention also relates to a method for surface-treating vulcanized rubber for its joining to other materials.

Among several known methods for surface treatment of objects is one which employs a low-pressure glow plasma. This method permits uniform surface treatment, but in its industrial application it needs a large-scale vacuum unit that produces a vacuum of 10 Torr or below. It also needs a high equipment cost and running cost for continuous treatment which is greatly affected by the life of the valve. Another disadvantage is the difficulty in applying to objects of rubber or plastics which contain a large amount of volatile matters. In a reduced pressure, these volatile matters evaporate and

release themselves from the surface, adversely affecting the desired object, performance, and function of plasma treatment.

There is disclosed in Japanese Patent Laid-Open Nos. 15171/1990, 48626/1990, 241739/1991 and 236475/1991 a method for treating the surface of an object with a glow plasma obtained under atmospheric pressure. This method is suitable for flat objects but is not suitable for objects in the form of lump, sphere, or powder.

Surface treatment of vulcanized rubber has been a common practice where it is necessary to combine vulcanized rubber with other materials (or rubber, metal, or plastics) for the production of composite materials or it is necessary to perform pretreatment on vulcanized rubber for its finish coating. There are several known methods for this purpose.

For example, one of such known methods is used to impart adhesion properties to the surface of vulcanized rubber. It consists of highly oxidizing the surface of vulcanized rubber with a strong acid or strong oxidizing agent, thereby forming minute cracks in the

entire surface. However, it suffers from drawbacks involved in using a strong acid or oxidizing agent which needs great handling precaution and seriously damages the properties of vulcanized rubber. In addition, the surface treatment by this method does not provide a sufficient adhesion strength.

There are other methods for the surface treatment of vulcanized rubber. For example, one method consists of treating vulcanized rubber with chlorine gas, and another method consists of treating vulcanized rubber with a pseudohalide compound (See Japanese Patent Publication No. 36910/1977.) These methods are designed to attack the double bonds in rubber, thereby forming Cl — groups which promote adhesion. If these methods are applied to vulcanized rubber to be combined with other materials (such as metal and resin) for the production of anti — vibration rubber, they bring about resinification of treated surface which degrades adhesion properties and heat resistance. And they bring about the yellowing of the treated surface which are serious in the finish coating of golf balls made of balata

(transpolyisoprene). They deteriorate the appearance of golf balls. In addition, chlorine gas and pseudohalogen compound are dangerous to the environment.

There is another method for surface treatment. It is a low-pressure glow plasma treating method. According to this method, the surface of vulcanized rubber is treated with O_2 or a mixture of O_2 and CF_4 for etching oxidation and activation. This method permits uniform surface treatment, but in its industrial application it needs a large-scale vacuum unit that produces a vacuum of 10 Torr or below. It also needs a high equipment cost and running cost for continuous treatment. In addition, treatment in a reduced pressure causes the vulcanized rubber to give off oil and water which interfere with the desired performance and function.

It is an object of the present invention to provide novel methods and apparatus for surface treatment, suitable for objects in the form of lump, sphere, or the like, and preferably enabling a simple and uniform treatment.

In particular it would be preferable to provide a simple method for the surface treatment of vulcanized rubber which imparts good adhesion properties to the surface of vulcanized rubber to be joined to other materials for the production of good composite materials.

According to the present invention, the surface treatment of an object e.g. in the form of lump or sphere (which is not flat nor straight) can be accomplished by a first method and apparatus defined below.

A method for surface treatment which comprises subjecting an object for surface treatment to an atmospheric pressure plasma while rolling or floating said object in an insulating vessel fed with a prescribed gas and provided on the outside thereof with electrodes for voltage application and grounding, said atmospheric pressure plasma occurring upon application of a voltage to said electrodes.

An apparatus for surface treatment which comprises an insulating vessel in which an object for surface treatment is placed, electrodes for voltage application and grounding

which are arranged on the outside of the insulating vessel, an electric source to apply a voltage to said electrodes, a means to supply a prescribed gas to said insulating vessel, and a means to roll or float said object in the insulating vessel, said electrodes generating an atmospheric pressure plasma upon application of a voltage thereto and said object placed in said insulating vessel being exposed to said atmospheric pressure plasma.

The present invention employs atmospheric pressure plasma for the surface treatment of a rolling or floating object. This permits uniform surface treatment for objects of any form. The resulting treated surface permits good adhesion of coating film or adhesive over the entire surface in the coating or bonding of rubber and plastics.

The surface treatment according to the present invention is by means of an atmospheric pressure discharge which takes place in a gaseous atmosphere, usually at 80-100°C. Therefore, the surface treatment can be carried out without thermal deformation even though objects are poor in heat resistance. In addition, the surface

treatment under the atmospheric pressure can be performed on rubber and plastics without evaporation of volatile matters contained therein.

Another advantage of the surface treatment with the plasma is accurate temperature control in the case where objects are exposed to a high temperature. This is because the temperature of objects is affected only a little by the plasma.

According to the present invention, the surface treatment of an object e.g. in the form of lump or sphere (which is not flat nor straight) can also be accomplished by a second method and apparatus defined below.

A method for surface treatment which comprises subjecting an object for surface treatment to an atmospheric pressure plasma while rolling or floating said object in an insulating vessel fed with a prescribed gas and provided on the outside and inside thereof with electrodes for voltage application, said atmospheric pressure plasma occurring upon application of a voltage to said electrodes.

An apparatus for surface treatment which comprises an insulating vessel in which an

object for surface treatment is placed, two electrodes which are arranged on the outside and inside of the insulating vessel, an electric source to apply a voltage to said electrodes, a means to supply a prescribed gas to said insulating vessel, and a means to roll or float said object in the insulating vessel, said electrodes generating an atmospheric pressure plasma upon application of a voltage thereto and said object placed in said insulating vessel being exposed to said atmospheric pressure plasma.

The second method and apparatus offer not only the same advantages as the first ones but also the following additional advantage. The electrodes arranged on both the outside and inside of the insulating vessel permit discharge to start at a very low voltage (as demonstrated in Example 6 given later).

Atmospheric pressure plasma treatment permits the surface of vulcanized rubber to be treated with a gas containing oxygen and halogen. Such surface treatment needs no solvent and hence presents no possibility of environmental

pollution. The surface treatment imparts much better adhesion properties to the surface of vulcanized rubber than in the case of surface treatment by the conventional method which employs a low-pressure glow plasma. Moreover, the surface treatment affects only a very thin surface layer, without any damage to the vulcanized rubber itself.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a partial longitudinal sectional view showing a surface-treating apparatus embodying the present invention.

Fig. 2 is a sectional view taken along the line A-A in Fig. 1.

Fig. 3 is a partial longitudinal sectional view showing another surface-treating apparatus;

Fig. 4 is a sectional view taken along the line B-B in Fig. 3.

Fig. 5 is a partial longitudinal sectional view showing another surface-treating apparatus;

Fig. 6 is a sectional view taken along the line C-C in Fig. 5.

Fig. 7 is a partial longitudinal sectional view showing another surface-treating apparatus;

Fig. 8 is a sectional view taken along the line D-D in Fig. 7.

Fig. 9 is a partial longitudinal sectional view showing another surface-treating apparatus;

Fig. 10 is a partial longitudinal sectional view showing another surface-treating apparatus;

Fig. 11 is a partial longitudinal sectional view showing another surface-treating apparatus;

Fig. 12 is a partial longitudinal sectional view showing another surface-treating apparatus;

Fig. 13 is a partial longitudinal sectional view showing another surface-treating apparatus;

Fig. 14 is a partial longitudinal sectional view showing another surface-treating apparatus;

Fig. 15 is a partial longitudinal sectional view showing another surface-treating

apparatus;

Fig. 16 is a sectional view taken along the line E－E in Fig. 15.

Fig. 17 is a partial longitudinal sectional view showing another surface－treating apparatus;

Fig. 18 is a sectional view taken along the line F－F in Fig. 17.

Fig. 19 is a sectional view showing another surface－treating apparatus;

Fig. 20 is a sectional view taken along the line G－G in Fig. 19.

Fig. 21 is a partial longitudinal sectional view showing a surface－treating apparatus;

Fig. 22 is a partial longitudinal sectional view showing a surface－treating apparatus;

Fig. 23 is a sectional view taken along the line H－H in Fig. 22.

Fig. 24 is a partial longitudinal sectional view showing another surface－treating apparatus;

Fig. 25 is a sectional view taken along

the line I—I in Fig. 24.

Fig. 26 is a partial longitudinal sectional view showing another surface—treating apparatus;

Fig. 27 is a sectional view taken along the line J—J in Fig. 26.

Fig. 28 is a partial longitudinal sectional view showing another surface—treating apparatus;

Fig. 29 is a sectional view taken along the line K—K in Fig. 28.

Fig. 30 is a partial longitudinal sectional view showing another surface—treating apparatus;

Fig. 31 is a sectional view taken along the line L—L in Fig. 30.

Fig. 32 is a partial longitudinal sectional view showing another surface—treating apparatus;

Fig. 33 is a sectional view taken along the line M—M in Fig. 32.

Fig. 34 is a partial longitudinal sectional view showing another surface—treating apparatus;

Fig. 35 is a sectional view taken along

the line N－N in Fig. 34.

Fig. 36 is a partial longitudinal sectional view showing another surface－treating apparatus;

Fig. 37 is a sectional view taken along the line O－O in Fig. 36.

Fig. 38 is a partial longitudinal sectional view showing another surface－treating apparatus;

Fig. 39 is a partial longitudinal sectional view showing another surface－treating apparatus;

Fig. 40 is a partial longitudinal sectional view showing another surface－treating apparatus;

Fig. 41 is a schematic diagram showing an atmospheric pressure plasma discharge unit;

Fig. 42 is a diagram illustrating the T－peel test used in Examples and Comparative Examples.

Fig. 43 is a diagram illustrating the 180° peel test used in Examples and Comparative Examples.

The present invention is embodied in a first method for surface treatment which comprises subjecting an object for surface treatment to an atmospheric pressure plasma in an insulating vessel fed with a prescribed gas and provided on the outside thereof with electrodes for voltage application and grounding, said atmospheric pressure plasma occurring upon application of a voltage to said electrodes.

The present invention is also embodied in a second method for surface treatment which comprises subjecting an object for surface treatment to an atmospheric pressure plasma in an insulating vessel fed with a prescribed gas and provided on the outside and inside thereof with electrodes for voltage application, said atmospheric pressure plasma occurring upon application of a voltage to said electrodes.

The object for surface treatment is not specifically restricted in shape so long as it is capable of rolling or floating in the

insulating vessel. It may be in the form of triangular lump, rectangular lump, polygonal lump (octahedron, dodecahedron, icosahedron, etc.), sphere, ellipsoid, or powder. In addition, it is not specifically restricted in material. It may be made from metal, metal compound, rubber, plastics, or ceramics.

The insulating vessel used in the present invention is not specifically restricted in material, size, and shape so long as it is capable of generating a plasma and rolling or floating an object therein for surface treatment. It may be made from glass, plastics or ceramics. For the uniform surface treatment of a spherical object, it should preferably be in the form of a cylinder large enough for the object to roll therein. The wall thickness of the insulating vessel should be smaller than 10 mm, preferably smaller than 3 mm.

The electrode for voltage application is not specifically restricted in size and shape so long as it is capable of generating a plasma.

Atmospheric pressure plasma for surface treatment is obtained stably by the aid of a

specific gas which facilitates the generation of atmospheric pressure discharge. Examples of the gas include inert gas (such as helium, argon, and neon), non-polymerizable gas (such as nitrogen and oxygen), and organic gas. They may be used alone or in combination with one another. Of these example, helium and neon are desirable. In the case where the object of surface treatment is to improve the adhesion properties of an object, the above-mentioned list may be expanded to include nitrogen gas, oxygen gas, halogen gas and halogen compound (such as chlorine, bromine, hydrogen chloride, hydrogen bromide, bromine cyanide, tin bromide, and carbon tetrafluoride), sulfur, sulfur trioxide, hydrogen sulfide, ammonia, carbon monoxide, carbon dioxide, and hydrogen. For the stable generation of atmospheric pressure plasma, these gases should be diluted with an inert gas which facilitates the generation of atmospheric pressure discharge.

It is not necessarily essential that these gases be gaseous at normal temperature. They should be fed in a proper way which is selected according to their state (solid, liquid, or gas)

at normal temperature and the temperature in the discharge region. Those which are gaseous at normal temperature or at a temperature in the discharge region may be introduced as such into the insulating vessel. Those which are liquid having a comparatively high vapor pressure may be introduced in the form of vapor or after bubbling with an inert gas. Those which are liquid having a comparatively low vapor pressure may be introduced after heating for evaporation or increasing the vapor pressure.

The pressure for generating a plasma is preferably in the range of about 200 Torr to about 3 atm, more desirably about 1 atm.

A variety of methods may be used for forming a plasma in the insulating vessel. In a first method, an AC voltage should be applied to the electrodes arranged on the outside of the insulating vessel. In a second method, either direct current and alternating current may be used for voltage application, with the latter being industrially desirable. The frequency should be higher than hundreds of hertz as in the ordinary AC discharge. The application of a voltage will

be explained below with reference to one example illustrated in Figs. 15 and 16. There are shown a cylindrical insulating vessel 1, an electrode 2c arranged on the outside thereof, and an electrode 2d arranged on the inside thereof. Voltage may be applied to either the outer electrode 2c or inner electrode 2d. That is, an AC voltage may be applied to the outer electrode 2c from an AC power source 3, as shown in Fig. 15. Alternatively, an AC voltage may be applied to the inner electrode 2d. The opposite electrode may or may not be grounded. In either case, it is possible to generate stable discharge at a low voltage.

What is important in the surface treatment with an atmospheric pressure plasma according to the present invention is to roll or float an object for surface treatment. The rolling of an object may be accomplished by inclining or swinging the cylindrical insulating vessel. The floating of an object may be accomplished by injecting a treating gas into the insulating vessel.

The above method can generate an atmospheric pressure glow plasma which gives the

best effect on surface treatment of a golf ball. However, in the present invention, an atmospheric pressure plasma may be generated by the other discharge methods including corona discharge, filament discharge and the like.

A preferred example of the apparatus used for surface treatment according to the first method of the present invention will be explained with reference to the accompanying drawings. Figs. 1 and 2 show an apparatus for the surface treatment of an spherical object 4 with a plasma. It is made up of an insulating vessel 1 and flat parallel electrodes 2a (for voltage application) and 2b (for grounding) across which a voltage is applied by an AC power source 3. Figs. 3 and 4 show an apparatus which is made up of an insulating vessel 1 and arched electrodes 2a and 2b arranged opposite to each other. Figs. 5 and 6 show an apparatus which is made up of an insulating vessel 1 and an elongate electrode 2′ spirally wound around the insulating vessel 1. A voltage is applied to one end of the electrode 2′ through a capacitor 5, with the other end grounded. Figs. 7 and 8 show an apparatus which is made up of an

insulating vessel 1 and annular electrodes 2a (for voltage application) and 2b (for grounding) which are arranged alternately at certain intervals. Fig. 9 shows an apparatus which is made up of elongate electrodes 2a (for voltage application) and 2b (for grounding) which are spirally wound around the insulating vessel at certain intervals.

Those apparatuses shown above permit a spherical object 4 to roll in the insulating vessel 1, as shown in Figs. 10 and 11. If the inside diameter of the insulating vessel 1 is close to the outside diameter of the spherical object 4, they permit the spherical object to roll smoothly without jams and minimize the diffusion of the treating gas (such as helium) into the atmosphere.

The apparatuses shown in Fig. 1 – 9 should preferably be arranged as shown in Figs. 10 – 14 for spherical objects which are rolled during surface treatment. Fig. 10 shows an apparatus which is provided with the electrodes shown in Figs. 7 and 8. It is designed such that the vessel 1 is inclined so that a spherical object 4 rolls down during surface treatment with an

atmospheric pressure plasma. The insulating vessel 1 is fed with a prescribed gas from a gas supply means (not shown) through a main gas inlet 6a. There are two auxiliary gas inlets 6b and 6b at the ends of the insulating vessel 1. This arrangement of gas inlets minimizes the diffusion of the gas into the atmosphere.

Fig. 11 shows an apparatus provided with the electrodes as shown in Figs. 7 and 8. This apparatus is designed such that one end of the insulating vessel 1 is fixed to a swinging mechanism 7 which swings so as to move the other end of the insulating vessel 1 up and down for the reciprocal movement of a spherical object in the insulating vessel during surface treatment. The treating gas is introduced into the insulating vessel 1 through a gas inlet 6 attached to the swinging mechanism 7. This arrangement minimizes the diffusion of the treating gas into the atmosphere.

Furthermore, Fig. 12 shows an apparatus provided with the electrodes as shown in Figs. 7 and 8. This apparatus is designed such that the insulating vessel 1 is held vertical, with the upper end thereof open and the lower end thereof

provided with a hinged door 8. The hinged door 8 is opened to place a spherical object 4 in the insulating vessel 1. This treating gas is introduced into the insulating vessel 1 so as to float and roll the spherical object 4 for surface treatment. It is important that the gap between the insulating vessel 1 and the spherical object 4 be properly controlled.

In the embodiments shown in Figs. 10 – 12 above, the apparatuses employ the electrodes shown in Figs. 7 and 8; however, they are illustrative only and it is possible to use other electrodes.

Fig. 10 shows an apparatus which is designed such that the surface treatment of an object with an atmospheric pressure plasma is carried out while the object is rolling in the insulating vessel. The apparatus shown in Fig. 10 may be modified such that the movement of an object may be accomplished by means of a belt conveyor as shown in Fig. 13.

The embodiment shown in Fig. 13 is provided with the electrodes shown in Figs. 1 and 2. The square cylindrical insulating vessel 1 is provided with gas inlets 6a and 6a and

curtains 10 and 10 at the ends of the insulating vessel 1. The curtains prevent the treating gas from diffusing into the atmosphere. The objects 4 and 4 for surface treatment are placed on a belt 12 and moved at a prescribed rate by a drive mechanism 11.

The embodiment shown in Fig. 14 is similar to that shown in Fig. 13. It is provided with gates 13 which divide the insulating vessel 1 into three compartments. The central compartment is provided with a main gas inlet 6a and the other compartments are provided with auxiliary gas inlets 6a and 6a.

A preferred example of the apparatus used for surface treatment according to the second method of the present invention will be explained with reference to Figs. 15 – 40.

Figs. 15 and 16 show an apparatus made up of a cylindrical insulating vessel 1 and an arched outer electrode 2c and an arched inner electrode 2d which are opposite to each other. A voltage is applied to the outer electrode 2c from an AC power source 3. Figs. 17 and 18 show an apparatus made up of an insulating vessel 1, two arched outer electrodes 2c and 2c opposite

to each other, and two inner arched electrodes 2d and 2d opposite to each other, with the outer and inner electrodes shifted 90° with respect to each other. Figs. 19 and 20 show an apparatus made up of an insulating vessel 1, elongate outer electrodes 2c arranged at certain intervals, and elongate inner electrodes 2d arranged at certain intervals. Fig. 21 shows an apparatus provided with nine outer electrodes 2c and nine inner electrodes 2d. Figs. 22 and 23 show an apparatus made up of an insulating vessel 1, a cylindrical outer electrode 2c surrounding the insulating vessel 1, and an elongate inner electrode 2d arranged in the insulating vessel 1. Figs. 24 and 25 show an apparatus made up of an insulating vessel 1, a cylindrical outer electrode 2c surrounding the insulating vessel, and three elongate inner electrodes 2d arranged at certain intervals in the insulating vessel 1. Figs. 26 and 27 show an apparatus made up of an insulating vessel 1, an elongate outer electrode 2c spirally wound around the insulating vessel 1 at certain intervals, and an elongate inner electrode 2d arranged in the insulating vessel 1. Figs. 28

and 29 show an apparatus made up of an insulating vessel 1, several ring-like outer electrodes 2c arranged at certain intervals, and an elongate inner electrode 2d arranged in the insulating vessel 1. Figs. 30 and 31 show an apparatus made up of an insulating vessel 1, a cylindrical outer electrode 2c surrounding the insulating vessel 1, and two elongate electrodes 2d and 2d arranged certain distance apart in the insulating vessel 1. The inner electrodes 2d and 2d function as a guide for the objects 4 to roll smoothly without jams. The inner electrodes 2d and 2d should preferably be positioned such that the objects 4 placed thereon are as close to the insulating vessel 1 as possible. Figs. 32 and 33 show an apparatus (similar to that shown in Figs. 30 and 31) which is designed such that five elongate inner electrodes 2d are arranged in a circle at certain intervals. An object 4 is placed in the space formed by these inner electrodes 2d.

Those embodiments shown in Figs. 15-33 are designed such that a voltage may be applied to either the outer electrode or the inner electrode. Those embodiments shown in Figs.

34 – 37 are designed such that a voltage is applied to the outer electrode. Figs. 34 and 35 show an apparatus made up of an insulating vessel 1 and ring – like outer electrodes 2c and ring – like inner electrodes 2d arranged at certain intervals. The inner electrodes 2d are left ungrounded. Figs. 36 and 37 show an apparatus made up of an insulating vessel 1 and oblique ring – like outer electrodes 2c and oblique ring – like inner electrodes 2d arranged at certain intervals. As in the case of the apparatus shown in Figs. 34 and 35, the inner electrodes 2d are left ungrounded.

To facilitate the rolling of objects for surface treatment in the apparatuses shown in Figs. 15 – 37, it is desirable to use an apparatus as shown in Figs. 38 and 39. The apparatus shown in Fig. 38 is provided with the electrodes as shown in Figs. 32 and 33. When in use, the apparatus permits an object 4 to roll through the insulating vessel 1 fixed inclined and undergo surface treatment by the atmospheric pressure plasma. The insulating vessel 1 is fed with a prescribed gas through a main gas inlet 6a at the center of the insulating vessel 1 from

a gas supply means (not shown). There are two auxiliary gas inlets 6b and 6b at the ends of the insulating vessel 1. This arrangement of gas inlets minimizes the diffusion of the gas into the atmosphere.

Fig. 39 shows an apparatus provided with the electrodes as shown in Figs. 15 and 16. This apparatus is designed such that one end of the insulating vessel 1 is fixed to a swinging mechanism 7 which swings so as to move the outer end of the insulating vessel 1 up and down for the reciprocal movement of an object 4. The treating gas is introduced into the insulating vessel 1 through a gas inlet 6 attached to the swinging mechanism 7. This arrangement minimizes the diffusion of the treating gas into the atmosphere.

Incidentally, although the apparatuses shown in Figs. 38 and 39 are provided with the electrodes shown in Figs. 32 – 33 and Figs. 15 – 16, it is also possible to use other electrodes. In the case of an apparatus as shown in Fig. 38, it is possible to perform surface treatment while moving an object by means of a belt conveyor.

Furthermore, Fig. 40 shows an apparatus provided with the electrodes as shown in Figs. 17 and 18. This apparatus is designed such that the insulating vessel 1 is held vertical, with the upper end thereof open and the lower end thereof provided with a hinged door 8. The hinged door 8 is opened to place an object 4 in the insulating vessel 1. The treating gas is introduced into the insulating vessel 1 through a gas inlet 6 at the bottom of the insulating vessel 1 so as to float and roll the object 4 for surface treatment. It is important that the gap between the insulating vessel 1 and the object 4 be properly controlled.

According to the method described above, it is possible to carry out the surface treatment of objects in the form of lump or sphere uniformly and certainly in a simple manner. The surface treatment is by means of the atmospheric pressure plasma which does not need the treating apparatus to be evacuated. The surface treatment at atmospheric pressure requires only a simple treating apparatus and can be applied to any objects without evaporation of volatile matters contained

therein.

The present invention also provides a method for surface treatment of vulcanized rubber. This method consists of treating the surface of vulcanized rubber with an atmospheric pressure plasma in the presence of a oxygen-containing gas and halogen-containing gases.

This method can be applied to any vulcanized rubber, which includes, for example, NR (natural rubber), SBR (styrene-butadiene rubber), IR (isoprene rubber), NBR (acrylonitrile butadiene rubber), EPM (ethylene propylene rubber), EPDM (ethylene propylene diene rubber), BR (butadiene rubber), IIR (butyl rubber), and CR (chloroprene rubber). The vulcanized rubber may be in any form, including plate, sheet, sphere, cylinder, column, and lump.

The surface treatment employs an oxygen-containing gas, which includes, for example, oxygen, water vapor, carbon dioxide, alcohols, ketones, and ethers. Of these gases, oxygen is preferable.

The surface treatment employs a halogen-containing

gas, which includes, for example, simple substance gas (such as F_2, Cl_2, Br_2, and I_2), hydrogen halide (such as HF, HCl, HBr, and HI), fluorocarbon (such as CF_4, $CClF_3$, CCl_2F_2, C_2F_6, and $CBrF_3$), halogenated hydrocarbon (such as $CHClF_2$, $CHBrF_2$, $CHCl_3$, CH_2Cl_2, CH_3CCl_3, and CCl_4), and SF_6. Of these examples, fluorocarbons and halogenated hydrocarbons are desirable from the standpoint of easy handling.

The following are some examples of the preferred combination of an oxygen-containing gas and a halogen-containing gas.

$O_2 + CCl_2F_2$, $O_2 + CClF_3$, $O_2 + CHClF_2$, $O_2 + CBrF_3$, $O_2 + CF_4$, $O_2 + CF_4 + CHCl_3$, $O_2 + CF_4 + CH_2Cl_2$, $O_2 + CF_4 + CCl_4$, $O_2 + CF_4 + CH_3CCl_3$

Any gas which contains both oxygen and halogen may be used alone.

These reactive gases for surface treatment should preferably be diluted with an inert gas which permits the atmospheric pressure glow discharge to take place easily. Examples of the inert gas include helium, argon, neon, nitrogen, hydrogen, and organic gases. They may be used alone or in combination with one another. Of these inert gases, helium is desirable.

It is not necessarily essential that these gases be gaseous at normal temperature. They should be fed in a proper way which is selected according to their state (solid, liquid, or gas) at normal temperature and the temperature in the discharge region. Those which are gaseous at normal temperature or at a temperature in the discharge region may be introduced as such into the insulating vessel. Those which are liquid having a comparatively high vapor pressure may be introduced in the form of vapor or after bubbling with an inert gas. The liquid may be applied directly to the surface of vulcanized rubber. Those which are liquid having a comparatively low vapor pressure may be introduced after heating for evaporation or increasing the vapor pressure.

The method for generating the atmospheric pressure plasma is not specifically limited so long as it is capable of generating glow discharge in the neighborhood of atmospheric pressure. Either direct current and alternating current may be used for voltage application, with the latter being industrially easy.

It is possible to generate the AC dis-

charge by using the ordinary inner electrodes. In this case, it is recommended that at least one of the electrodes be coated with an insulator so as to facilitate the stable generation of atmospheric pressure plasma. It is also possible to generate the AC discharge by using the outer electrodes if the treating chamber is made of insulator (such as glass). It is also possible to generate the AC discharge by using coils or waveguides. Incidentally, in the case of DC discharge, it is recommended that both electrodes (for voltage application and grounding) be not coated with an insulator so that a stable DC glow is generated by the direct flow of electrons from the electrode.

To practice the surface treatment, apparatus as shown in Fig. 41 is usable. This apparatus is made up of a treating chamber 101 and electrodes 104 and 104 arranged therein which generate the region of plasma discharge. An object for surface treatment is placed between the electrodes. The treating chamber 101 is fed with an oxygen-containing gas, a halogen-containing gas, and a diluent gas through a gas supply pipe

103. Simultaneously with the gas supply, the region of plasma discharge is generated between the electrodes 104 and 104. Incidentally, the electrodes 104 and 104 are coated with an insulator and spaced opposite to each other at a certain distance, with one of them being connected to an AC voltage 105 and the other being grounded. The surface treatment of an object 102 (vulcanized rubber) takes place in the space between the electrodes 104 and 104. The exhaust gas is discharged through a discharge pipe 106.

The surface treatment makes the surface of vulcanized rubber highly adhesive. Therefore, the surface-treated vulcanized rubber can be easily bonded to other materials by heating or pressing or both, which is a well-known bonding method.

Other materials to be bonded may be those of plastics, rubber, metal, or ceramics, in any form (such as plate, sheet, fiber, and lump).

The bonding of the surface-treated vulcanized rubber to other materials is facilitated by the aid of an adhesive, such as

silane coupling agent, aminosilane coupling agent, epoxy adhesive, urethane adhesive, phenol adhesive, acrylic adhesive, and rubber adhesive. A proper adhesive should be selected according to the kind and surface state of the adherents and the method of bonding. No adhesives may be necessary under certain circumstances.

The surface-treating method may be applicable to the production of a composite material of vulcanized rubber, especially to the production of golf balls, anti-vibration rubber, and reclaimed tires.

The present invention may be practised in a simple manner for the surface treatment of vulcanized rubber in a clean environment. After surface treatment, the vulcanized rubber has a much better adhesive surface than that treated with a low-pressure glow plasma. The surface treatment affects only a very thin surface layer, without deteriorating the physical properties of the vulcanized rubber.

EXAMPLE

The invention will be described in more

detail with reference to the following examples, which are not intended to restrict the scope of the invention.

Example 1

Using an apparatus as shown in Fig. 10, surface treatment was performed on a spherical object of polypropylene resin (40 mm in diameter). The glass insulating vessel 1 (1500 mm long and 45 mm in inside diameter) inclined 25° was filled with helium gas containing 1% oxygen introduced through the gas inlet 6a. The insulating vessel 1 was further supplied with helium gas containing 1% oxygen through the gas inlets 6b located at both ends thereof, so that the helium gas leaks slightly from the open ends which serve as the entrance and exit of the object. An AC voltage (4 kV, 5 kHz) was applied across the electrodes 2a and 2b so as to produce an atmospheric pressure plasma in the vessel 1. The spherical object of polypropylene resin 4 was allowed to roll through the vessel 1 from one open end to the other for the surface treatment. For comparison, the same procedure as mentioned above was repeated except that the

vessel 1 was kept horizontal so that the object 4 remained at rest at the center of the vessel 1. Three samples, one rolled during surface treatment, one kept at rest during surfaee treatment, and one not surface-treated, were tested for surface properties by measuring the contact angle of water at different positions. The results are shown in Table 1.

Table 1

	Rolled	Not rolled	Not treated
Upper part	35°	39°	110°
Front part	36°	46°	109°
Rear part	35°	45°	112°
Left part	38°	36°	110°
Right part	40°	38°	110°
Lower part	38°	110°	112°
Average	37°	52.3°	110.5°

It is noted from Table 1 that the object undergoes uniform surface treatment when it is

rolled but the object does not when it is not rolled.

Example 2

The same procedure as in Example 1 was repeated except that helium was introduced through the gas inlets 6a and 6b and the object was replaced by a two-piece solid golf ball (43 mm in diameter) having a covering layer of thermoplastic ionomer resin in which dimples are formed.

After surface treatment, the golf ball was coated with a paint, followed by drying. The adhesion of the coating film was evaluated by cross-hatch test and repeated ball impact test. The results are shown in Table 2. For comparison, the same procedure as mentioned above was repeated except that the surface coating was not performed. The results are also shown in Table 2.

The cross-hatch test consists of cutting the coating film into small pieces in mutually perpendicular directions, applying a piece of adhesive cellophane tape over the cut coating film, rapidly pulling off the tape, and counting

the number of pieces removed.

The repeated impact test consists of subjecting the finished golf ball to impact repeatedly and visually examining the coating film for peeling from the golf ball.

Table 2

	Treated ball (Example)	Untreated ball (Comparative Example)
Cross-hatch test	None peeled out of 10.	9 pieces peeled out of 10.
Repeated impact test	No peeling after 100 repetitions.	Peeling after 20 repetitions.

Example 3

The same procedure as in Example 1 was repeated for the surface treatment of a golf ball except that the electrode was replaced by the one shown in Figs. 5 and 6 and a high-frequency voltage (13.56 MHz, 100 W) was applied across the electrodes. The results were identical with those shown in Table 2.

Example 4

Using an apparatus shown in Fig. 11, the surface treatment and coating of golf balls were carried out under the same conditions as in Example 2 except that the vessel 1 was swung 6 times per minute, with the maximum slope being 30°. The results were identical with those shown in Table 1.

Example 5

Using an apparatus shown in Fig. 12, the surface treatment and coating of golf balls were carried out under the same conditions as in Example 2 except that helium gas was injected into the vessel 1 through the inlet 6 so that the golf ball 4 floated in the vessel 1. The results were identical with those shown in Table 2.

Example 6

Using an electrode as shown in Figs. 22 and 23 or an electrode as shown in Figs. 3 and 4, discharging was carried out under the following conditions to compare their discharge starting voltage. The results are shown in Table 3.

Dimensions of the electrodes as shown in Figs. 22 and 23

Insulating vessel: glass, 1500 mm long, 50 mm in outside diameter, 45 mm in inside diameter

Outer electrode: stainless steel, 240 mm long

Inner electrode: stainless steel, 240 mm long, 6 mm in diameter

AC frequency: 5 kHz

Dimensions of the electrodes as shown in Figs. 3 and 4

Insulating vessel: the same as above

Two outer electrodes: stainless steel, 240 mm long, with a minimum distance of 7 mm between electrodes

AC frequency: 5 kHz

Table 3

Electrode and mode			Discharge start voltage (V)
	Outer electrode	Inner electrode	
Electrode as shown in Figs. 22 and 23.	AC applied	Grounded	1300
	AC applied	Not grounded	1300
	Grounded	AC applied	1100
	Not grounded	AC applied	1100
Electrode as shown in Figs. 3 and 4.			2450

It is noted from Table 3 that it is possible to lower the discharge start voltage if the electrodes are arranged on both outside and inside of the insulating vessel. It is also noted that the discharge start voltage is slightly higher when an AC voltage is applied to the outer electrode than when an AC voltage is applied to the inner electrode. Nevertheless, it is still lower than in the case where the two electrodes are all arranged on the outside. In addition, it is noted that the discharge was stable regardless of grounding.

Example 7

Using an apparatus as shown in Fig. 38, surface treatment was performed on a two-piece solid golf ball (43 mm in diameter) having a covering layer of thermoplastic ionomer resin in which dimples are formed. The glass insulating vessel 1 (1500 mm long and 45 mm in inside diameter) inclined 25° was filled with helium gas introduced through the gas inlet 6a. The insulating vessel 1 was further supplied with helium gas through the gas inlets 6b located at both ends thereof, so that the helium gas leaks slightly from the open ends which serve as the entrance and exit of the golf ball. An AC voltage (4 kV, 5kHz) was applied across the electrodes 2c and 2d so as to produce an atmospheric pressure plasma in the vessel 1. A golf ball 4 was allowed to roll slowly through the vessel 1 from one open end to the other over five minutes during which the surface coating was accomplished.

After surface treatment, the golf ball was coated with a clear polyurethane paint, followed by drying. The adhesion of the coating film was evaluated by cross-hatch test and repeated ball impact test. The results are shown in Table 4.

For comparison, the same procedure as mentioned above was repeated except that the surface coating was not performed. The results are also shown in Table 4.

The cross－hatch test consists of cutting the coating film into small pieces in mutually perpendicular directions, applying a piece of adhesive cellophane tape over the cut coating film, rapidly pulling off the tape, and counting the number of pieces removed.

The repeated impact test consists of subjecting the finished golf ball to impact repeatedly and visually examining the coating film for peeling from the golf ball.

Table 4

	Treated ball (Example)	Untreated ball (Comparative Example)
Cross－hatch test	None peeled out of 10.	9 pieces peeled out of 10.
Repeated impact test	No peeling after 100 repetitions.	Peeling after 20 repetitions.

Example 8

The same procedure as in Example 6 was

repeated except that the electrode was replaced by the one shown in Figs. 17 and 18 and a high-frequency voltage (13.56 MHz, 100 W) was applied across the electrodes. The results were identical with those shown in Table 4.

Example 9

Using an apparatus shown in Fig. 39, the surface treatment and coating of golf balls were carried out under the same conditions as in Example 7. The vessel 1 was swung 6 times per minute, with the maximum slope being 30°. The results were identical with those shown in Table 4.

Examples 10 – 23 and Comparative Examples 1 – 12

Using an apparatus for atmospheric pressure plasma discharge shown in Fig. 41, surface treatment was performed under the conditions shown in Table 5 on vulcanized rubber prepared from a rubber compound specified below. After surface treatment, the vulcanized rubber was tested for physical properties (Examples 10 – 23). For comparison, the same experiment as above was performed on a sample of vulcanized

rubber without surface treatment (Comparative Example 1), a sample of vulcanized rubber treated with a pseudohalogen compound (Comparative Example 2), and samples of vulcanized rubber treated with a low-pressure glow plasma (Comparative Examples 3-12). The results are shown in Table 5.

Experiment 1

	pbw
Transpolyisoprene	30
SBR	50
(#1502, made by Japan Synthetic Rubber)	
NR	20
Sulfur	1
Zinc oxide	5
Nocrac NS-6	1
(made by Ouchi Shinko Kagaku Kogyo)	

A rubber compound specified above was vulcanized, and the vulcanized rubber was made into test pieces measuring 10 × 60 × 3 mm. The test pieces (in Examples 10-18 and Comparative Examples 1-7) underwent surface treatment under the conditions shown in Table 5. The treated surface was coated with a urethane adhesive, and

two test pieces were bonded together, with the coating inside. The bonded test piece underwent T-peel test as shown in Fig. 42 to measure the bond strength. In Fig. 42, the reference numeral 107 represents the vulcanized rubber test piece and the reference numeral 108 represents the urethane adhesive.

Experiment 2

Vulcanized rubbers (in Examples 11-18) underwent the surface treatment under the same conditions as in Experiment 1. The treated surface of the test piece was coated with a urethane adhesive and bonded to a piece of polyester nonwoven fabric. The resulting sample underwent 180° peel test as shown in Fig. 43 to measure the bond strength. In Fig. 43, the reference numeral 109 represents the nonwoven fabric.

Experiment 3

	pbw
SBR	50
(#1502, made by Japan Synthetic Rubber)	
NR	50

Carbon black	60
Sulfur	2
Zinc oxide	5
Antioxidant (*1)	1
Accelerator (*2)	1

(*1) N,N'−diphenyl−p−phenylenediamine (DPPD)

(*2) N−oxydiethylene−2−benzothiazole (NOBS)

A rubber compound specified above was vulcanized, and the vulcanized rubber was made into test pieces measuring 34 × 75 × 5 mm. The test pieces (in Examples 12−18 and Comparative Examples 1, 2, 4−7) underwent surface treatment under the conditions shown in Table 5. The treated surface was coated with a phenol adhesive, and two test pieces were bonded together, with the coating inside, under pressure at 150℃ for 30 minutes. The bonded test piece underwent T−peel test as shown in Fig. 42 to measure the bond strength.

Experiment 4

	pbw
NBR (N2305, made by Japan Synthetic Rubber)	100
Carbon black	60

Sulfur	2
Zinc oxide	5
Antioxidant (*3)	1
Accelerator (*4)	1
Mineral oil	2

(*3) N－phenyl－N′－isopropyl－p－phenylenediamine (NOCRAC 810－NA)

(*4) Tetramethylthiuram monosulfide (TMTM)

A rubber compound specified above was vulcanized at 150℃ for 20 minutes, and the vulcanized rubber was made into test pieces measuring 34 × 75 × 5 mm. The test pieces (in Examples 17－23 and Comparative Examples 10－14) underwent surface treatment under the conditions shown in Table 5. The treated surface was coated with a phenol adhesive, followed by heating in an oven at 150℃ for 30 minutes. Using a resin injection machine, glass fiber－filled nylon (50%) was injection molded on the phenolic resin adhesive. The resulting sample underwent the 180° peel test as shown in Fig. 43 and the area (in terms of %) in which the rubber ruptured was measured.

Table 5

Example	Treatment	Pressure (Torr)	Reactive gas	Diluent gas	Treating time (min.)	Bond strength (kgf/cm)			Rubber rupture
						Experiment 1	Experiment 2	Experiment 3	Experiment 4
10	Atmospheric pressure plasma treatment	760	O_2, SF_6	He	5	2.7	—	—	—
11		760	O_2, CF_4	He	5	4.7	2.0	—	—
12		760	O_2, $CClF_3$	He	5	8.6	6.9	12.5	—
13		760	O_2, $CHClF_2$	He	5	8.0	7.2	10.9	—
14		760	O_2, CCl_2F_2	He	5	9.4	7.6	10.6	—
15		760	O_2, CF_4, $CHCl_3$	He	5	3.6	3.0	9.4	—
16		760	O_2, CF_4, CH_2Cl_2	He	5	8.7	7.1	6.8	—
17		760	O_2, CF_4, CH_3CCl_3	He	5	8.1	7.0	7.6	—
18		760	O_2, $CBrF_3$	He	5	7.6	6.1	9.4	—
19		760	O_2, CF_4	He	0.5	—	—	—	100
20		760	O_2, CF_4	He	1	—	—	—	100
21		760	O_2, CF_4	He	2	—	—	—	100
22		760	O_2, CF_4	He	5	—	—	—	100
23		760	O_2, CF_4	He	10	—	—	—	100

Table 5 (Contd.)

Comparative Example	Treatment	Pressure (Torr)	Reactive gas	Diluent gas	Treating time (min.)	Bond strength (kgf/cm)			Rubber rupture (%)
						Experiment 1	Experiment 2	Experiment 3	Experiment 4
1	None	—	—	—	—	0.0	0.0	0.0	—
2	Pseudo-halogen compound	—	—	—	—	7.8	6.4	9.1	—
3	Low-pressure glow plasma treatment	1.0	O_2, SF_6	—	5	1.3	—	—	—
4		1.0	O_2, SF_4	—	5	0.6	—	2.0	—
5		1.0	O_2, $CClF_3$	—	5	1.8	—	1.2	—
6		1.0	O_2, $CHClF_2$	—	5	2.6	—	1.0	—
7		1.0	O_2, CCl_2F_2	—	5	3.8	—	1.4	—
8		1.0	O_2, CF_4	—	0.5	—	—	—	50
9		1.0	O_2, CF_4	—	1	—	—	—	70
10		1.0	O_2, CF_4	—	2	—	—	—	80
11		1.0	O_2, CF_4	—	5	—	—	—	10
12		1.0	O_2, CF_4	—	10	—	—	—	0

It is noted from Table 5 that in the case of low-pressure plasma treatment (Comparative Examples 8 to 12), the area of rubber rupture increases in proportion to the treating time (in the range of from 0.5 to 2 minutes), whereas it decreases when the treating time exceeds 2 minutes. This leads to poor adhesion. In addition, the area of rubber rupture does not reach 100% even in the case of treatment for 2 minutes which should give the highest value of rubber rupture. By contrast, in the case of atmospheric pressure plasma treatment (Examples 19 to 23), the treatment for 0.5 minute is enough for the rubber rupture to reach 100%. Prolonged treating time does not affect the adhesion properties. The conceivable reason for this is as follows: In the case of low-pressure glow plasma treatment, the rubber is exposed to a plasma atmosphere for a long time under reduced pressure, and consequently the rubber gets hot and gives off a gas which prevents the surface treatment. By contrast, in the case of atmospheric pressure plasma treatment, the rubber is not placed in an atmosphere under reduced pressure, and consequently the

rubber does not give off a gas which prevents the stable surface treatment.

CLAIMS:

1. A method for surface treatment which comprises subjecting an object for surface treatment to an atmospheric pressure plasma while rolling or floating said object in an insulating vessel fed with a prescribed gas and provided on the outside thereof with electrodes for voltage application and grounding, said atmospheric pressure plasma occurring upon application of a voltage to said electrodes.

2. A method for surface treatment which comprises subjecting an object for surface treatment to an atmospheric pressure plasma while rolling or floating said object in an insulating vessel fed with a prescribed gas and provided on the outside and inside thereof with electrodes for voltage application, said atmospheric pressure plasma occurring upon application of a voltage to said electrodes.

3. The method for surface treatment as defined in Claim 1 or 2, wherein the atmospheric pressure plasma is an atmospheric pressure glow plasma.

4. The method for surface treatment as

defined in Claim 1 or 2, wherein the pressure for generating plasma is in the range of about 200 Torr to about 3 atm.

5. An apparatus for surface treatment which comprises an insulating vessel in which an object for surface treatment is placed, electrodes for voltage application and grounding which are arranged on the outside of the insulating vessel, an electric source to apply a voltage to said electrodes, a means to supply a prescribed gas to said insulating vessel, and a means to roll or float said object in the insulating vessel, said electrodes generating an atmospheric pressure plasma upon application of a voltage thereto and said object placed in said insulating vessel being exposed to said atmospheric pressure plasma.

6. An apparatus for surface treatment which comprises an insulating vessel in which an object for surface treatment is placed, two electrodes which are arranged on the outside and inside of the insulating vessel, an electric source to apply a voltage to said electrodes, a means to supply a prescribed gas to said insulating vessel, and a means to roll or float

said object in the insulating vessel, said electrodes generating an atmospheric pressure plasma upon application of a voltage thereto and said object placed in said insulating vessel being exposed to said atmospheric pressure plasma.

7. The apparatus for surface treatment as defined in Claim 5 or 6, wherein the atmospheric pressure plasma is an atmospheric pressure glow plasma.

8. A method for the surface treatment of vulcanized rubber which comprises performing the atmospheric pressure plasma treatment on the surface of vulcanized rubber in the presence an oxygen — containing gas and halogen — containing gases.

9. A surface-treated article obtainable in accordance with any one of claims 1 to 4.

10. A method, apparatus or article surface-treated substantially as described herein with reference to the Examples and drawings, but not the Comparative Examples.

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Patents Act 1977
[aminer's report to the Comptroller under Section 17 (The Search Report)

Application number

GB 9217744.3

Relevant Technical fields

(i) UK Cl (Edition K) H1D - DGQ, DGP; H1X - X5G; C3L - LJE, LJX

(ii) Int Cl (Edition 5) H01J; H01T; H05H; C08J

Search Examiner

R H LITTLEMORE

Databases (see over)

(i) UK Patent Office

(ii)

Date of Search

30 NOVEMBER 1992

Documents considered relevant following a search in respect of claims 1-10

Category (see over)	Identity of document and relevant passages		Relevant to claim(s)
Y	GB 2164947 A	(BRIDGESTONE CORP) Whole document, eg. see Figures 1, 4	1, 2, 5, 6, 8, 9
Y	GB 2059971 A	(E A DUKHOVESKOI ETC) See Figures 1 and 3	5, 6, 8, 9
X	EP 0431951 A2	(RES DEV CORP OF JAPAN) Whole document, eg. Figure 1, Claim 1 and column 4 line 15 to column 5 line 14	1-7
X	EP 0267513 A2	(SEMI CONDUCTER ENERGY) Whole document, eg. Figure 4 and column 5 lines 17-51	1-7
Y	EP 0202636 A2	(SHIN-ETSU) eg. See Claim 1	1, 2, 8
X	EP 0178907 A2	(SANKYO DENGYO) Whole document, eg. see Figures 2, 13, 23, 26-28 and page 23 1st paragraph to page 25 1st paragraph	1-9
X	EP 0171239 A1	(SANKYO DENGYO) Whole document, eg. Figures 1, 2 and page 5 line 24 to page 6 line 9	1-9

Category	Identity of document and relevant passages	Relevant to clai[m(s)]

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(ii) Int Cl (Edition)

Databases (see over)

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Search Examiner

R H LITTLEMORE

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30 NOVEMBER 1992

Documents considered relevant following a search in respect of claims

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
Y	EP 0046945 A1 (TOKYO SHIBAURA) eg. See Figures 1, 2	1, 2, 5, 6
X	US 4724508 (MACY) Whole document, eg. See Figures 1, 6 and 7	1-7

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